

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
28 March 2002 (28.03.2002)

PCT

(10) International Publication Number
WO 02/24329 A2

- (51) International Patent Classification⁷: B01J 29/00
- (21) International Application Number: PCT/US01/29701
- (22) International Filing Date:
21 September 2001 (21.09.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
09/667,677 22 September 2000 (22.09.2000) US
09/956,250 20 September 2001 (20.09.2001) US
- (71) Applicant: ENGELHARD CORPORATION [US/US];
101 Wood Avenue, P.O. Box 770, Iselin, NJ 08830-0770 (US).
- (72) Inventors: STOCKWELL, David, M.; 202 Ashland Road, Middlesex, NJ 08846 (US). BROWN, Randall, P.; 2604 Hilltop Court, Macon, GA 31217 (US).
- (74) Agents: MILLER, Stephen, I. et al.; Engelhard Corporation, 101 Wood Avenue, P.O. Box 770, Iselin, NJ 08830-0770 (US).
- (81) Designated States (*national*): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Declaration under Rule 4.17:**
— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for all designations*
- Published:**
— *without international search report and to be republished upon receipt of that report*
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: STRUCTURALLY ENHANCED CRACKING CATALYSTS

(57) Abstract: Zeolite microsphere FCC catalysts having a novel morphology comprising a macroporous matrix and crystallized zeolite freely coating the walls of the pores of the matrix. The catalysts are formed from microspheres containing a metakaolin and kaolin calcined through its exotherm, the latter calcined kaolin being derived from a kaolin having a high pore volume. Kaolin having a high pore volume can be a pulverized ultrafine kaolin or a kaolin which has been pulverized to have an incipient slurry point less than 57 % solids.

WO 02/24329 A2

STRUCTURALLY ENHANCED CRACKING CATALYSTS

CROSS-REFERENCE TO RELATED APPLICATIONS

5 This application is a continuation-in-part of U.S. rial
No. 09/667,677, filed September 22, 2000.

BACKGROUND OF THE INVENTION

10 The present invention relates to novel fluid catalytic
cracking catalysts comprising microspheres containing Y-
faujasite zeolite and having exceptionally high activity and
other desirable characteristics, methods for making such
catalysts and the use of such catalysts for cracking
petroleum feedstocks, particularly under short residence
15 time processes.

 Since the 1960's, most commercial fluid catalytic
cracking catalysts have contained zeolites as an active
component. Such catalysts have taken the form of small
particles, called microspheres, containing both an active
20 zeolite component and a non-zeolite component. Frequently,
the non-zeolitic component is referred to as the matrix for
the zeolitic component of the catalyst. The non-zeolitic
component is known to perform a number of important
functions, relating to both the catalytic and physical
25 properties of the catalyst. Oblad described those functions
as follows:

 "The matrix is said to act as a sink for sodium in the
sieve thus adding stability to the zeolite particles in
the matrix catalyst. The matrix serves the additional
30 function of: diluting the zeolite; stabilizing it
towards heat and steam and mechanical attrition;
providing high porosity so that the zeolite can be used

to its maximum capacity and regeneration can be made easy; and finally it provides the bulk properties that are important for heat transfer during regeneration and cracking and heat storage in large-scale catalytic cracking." A.G. Oblad Molecular Sieve Cracking Catalysts, The Oil And Gas Journal, 70, 84 (March 27, 1972).

In prior art fluid catalytic cracking catalysts, the active zeolitic component is incorporated into the microspheres of the catalyst by one of two general techniques. In one technique, the zeolitic component is crystallized and then incorporated into microspheres in a separate step. In the second technique, the in-situ technique, microspheres are first formed and the zeolitic component is then crystallized in the microspheres themselves to provide microspheres containing both zeolitic and non-zeolitic components.

It has long been recognized that for a fluid catalytic cracking catalyst to be commercially successful, it must have commercially acceptable activity, selectivity, and stability characteristics. It must be sufficiently active to give economically attractive yields, it must have good selectivity towards producing products that are desired and not producing products that are not desired, and it must be sufficiently hydrothermally stable and attrition resistant to have a commercially useful life.

Two products that are particularly undesirable in commercial catalytic cracking processes are coke and hydrogen. Even small increases in the yields of these products relative to the yield of gasoline can cause significant practical problems. For example, increases in the amount of coke produced can cause undesirable increases

in the heat that is generated by burning off the coke during the highly exothermic regeneration of the catalyst.

Conversely, insufficient coke production can also distort the heat balance of the cracking process. In addition, in commercial refineries, expensive compressors are used to handle high volume gases, such as hydrogen. Increases in the volume of hydrogen produced, therefore, can add substantially to the capital expense of the refinery.

U.S. Patent No. 4,493,902, the teachings of which are incorporated herein by cross-reference, discloses novel fluid cracking catalysts comprising attrition-resistant, high zeolitic content, catalytically active microspheres containing more than about 40%, preferably 50-70% by weight Y faujasite and methods for making such catalysts by crystallizing more than about 40% sodium Y zeolite in porous microspheres composed of a mixture of two different forms of chemically reactive calcined clay, namely, metakaolin (kaolin calcined to undergo a strong endothermic reaction associated with dehydroxylation) and kaolin clay calcined under conditions more severe than those used to convert kaolin to metakaolin, i.e., kaolin clay calcined to undergo the characteristic kaolin exothermic reaction, sometimes referred to as the spinel form of calcined kaolin. In a preferred embodiment, the microspheres containing the two forms of calcined kaolin clay are immersed in an alkaline sodium silicate solution, which is heated, preferably until the maximum obtainable amount of Y faujasite is crystallized in the microspheres.

In practice of the '902 technology, the porous microspheres in which the zeolite is crystallized are preferably prepared by forming an aqueous slurry of powdered raw (hydrated) kaolin clay ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) and powdered

calcined kaolin clay that has undergone the exotherm together with a minor amount of sodium silicate which acts as fluidizing agent for the slurry that is charged to a spray dryer to form microspheres and then functions to provide physical integrity to the components of the spray dried microspheres. The spray dried microspheres containing a mixture of hydrated kaolin clay and kaolin calcined to undergo the exotherm are then calcined under controlled conditions, less severe than those required to cause kaolin to undergo the exotherm, in order to dehydrate the hydrated kaolin clay portion of the microspheres and to effect its conversion into metakaolin, this resulting in microspheres containing the desired mixture of metakaolin, kaolin calcined to undergo the exotherm and sodium silicate binder. In illustrative examples of the '902 patent, about equal weights of hydrated clay and spinel are present in the spray dryer feed and the resulting calcined microspheres contain somewhat more clay that has undergone the exotherm than metakaolin. The '902 patent teaches that the calcined microspheres comprise about 30-60% by weight metakaolin and about 40-70% by weight kaolin characterized through its characteristic exotherm. A less preferred method described in the patent, involves spray drying a slurry containing a mixture of kaolin clay previously calcined to metakaolin condition and kaolin calcined to undergo the exotherm but without including any hydrated kaolin in the slurry, thus providing microspheres containing both metakaolin and kaolin calcined to undergo the exotherm directly, without calcining to convert hydrated kaolin to metakaolin.

In carrying out the invention described in the '902 patent, the microspheres composed of kaolin calcined to undergo the exotherm and metakaolin are reacted with a

caustic enriched sodium silicate solution in the presence of a crystallization initiator (seeds) to convert silica and alumina in the microspheres into synthetic sodium faujasite (zeolite Y). The microspheres are separated from the sodium silicate mother liquor, ion-exchanged with rare earth, ammonium ions or both to form rare earth or various known stabilized forms of catalysts. The technology of the '902 patent provides means for achieving a desirable and unique combination of high zeolite content associated with high activity, good selectivity and thermal stability, as well as attrition-resistance.

The aforementioned technology has met widespread commercial success. Because of the availability of high zeolite content microspheres which are also attrition-resistant, custom designed catalysts are now available to oil refineries with specific performance goals, such as improved activity and/or selectivity without incurring costly mechanical redesigns. A significant portion of the FCC catalysts presently supplied to domestic and foreign oil refiners is based on this technology. Refineries whose FCC units are limited by the maximum tolerable regenerator temperature or by air blower capacity seek selectivity improvements resulting in reductions in coke make while the gas compressor limitations make catalysts that reduce gas make highly desirable. Seemingly a small reduction in coke can represent a significant economic benefit to the operation of an FCC unit with air blower or regenerator temperature limitations.

Improvements in cracking activity and gasoline selectivity of cracking catalysts do not necessarily go hand in hand. Thus, a cracking catalyst can have outstandingly high cracking activity, but if the activity results in a

high level of conversion to coke and/or gas at the expense of gasoline the catalyst will have limited utility. Catalytic cracking activity in present day FCC catalysts is attributable to both the zeolite and non-zeolite (e.g.,
5 matrix) components. Zeolite cracking tends to be gasoline selective. Matrix cracking tends to be less gasoline selective. After appropriate ion-exchange treatments with rare earth cations, high zeolite content microspheres produced by the in situ procedure described in the '902
10 patent are both highly active and highly gasoline selective. As zeolite content of these unblended microspheres is increased, both activity and selectivity tend to increase. This may be explained by the decrease in matrix content with increase in zeolite content and the decreasingly prominent
15 role of nonselective matrix cracking. Thus, increases in the zeolite content of the high zeolite content microspheres have been reported to be highly desirable.

The activity and selectivity characteristics of the catalysts formed by the process of the '902 patent are
20 achieved even though, in general, the catalysts have relatively low total porosity as compared to fluid catalytic cracking catalysts prepared by incorporating the zeolite content into a matrix. In particular, the microspheres of such catalysts, in some cases, have a total porosity of less
25 than about 0.15 cc/g. or even less than about 0.10 cc/g. In general, the microspheres of the '902 patent have a total porosity of less than 0.30 cc/g. As used herein, "total porosity" means the volume of pores having diameters in the range of 35-20,000Å, as determined by the mercury
30 porosimetry technique. The '902 patent noted that it was surprising that microspheres having a total porosity of less than about 0.15 cc/g. exhibit the activity and selectivity

characteristics found. For example, such a result is contrary to the prior art disclosures that low pore volumes "can lead to selectivity losses due to diffusional restrictions."

5 It is believed that the relatively low porosity of the catalyst microspheres formed as in the '902 patent does not adversely effect activity and selectivity characteristics, since the microspheres of the '902 patent are not diffusion limited relative to the typical FCC processing conditions
10 which were used at the time of the patent. In particular, catalyst contact time with the feed to be cracked was typically 5 seconds or more. Thus, while typical FCC catalysts formed by mechanically incorporating the zeolite within a matrix may have been more porous, the reaction time
15 in prior art FCC risers did not yield any advantage in activity or selectivity. This result inspired the conclusion that transport processes were not at all limiting in FCC catalysts, at least outside the zeolite structure. Assertions made to the contrary were inconsistent with the
20 facts and easily dismissed as self-serving. Importantly, the attrition resistance of the microspheres prepared in accordance with the '902 patent was superior to the conventional FCC catalysts in which the crystallized zeolite catalytic component was physically incorporated into the
25 non-zeolitic matrix.

Recently, however, FCC apparatus have been developed which drastically reduce the contact time between the catalyst and the feed which is to be cracked. Conventionally, the reactor is a riser in which the catalyst
30 and hydrocarbon feed enter at the bottom of the riser and are transported through the riser. The hot catalyst effects cracking of the hydrocarbon during the passage through the

riser and upon discharge from the riser, the cracked products are separated from the catalyst. The catalyst is then delivered to a regenerator where the coke is removed, thereby cleaning the catalyst and at the same time providing the necessary heat for the catalyst in the riser reactor. The newer riser reactors operate at lower residence time and higher operating temperatures to minimize coke selectivity and delta coke. Several of the designs do not even employ a riser, further reducing contact time to below one second.

Gasoline and dry gas selectivity can improve as a result of the hardware changes. These FCC unit modifications are marketed as valuable independent of the type of catalyst purchased, implying an absence of systematic problems in state of the art catalyst technology.

The processing of increasingly heavier feeds in FCC type processes and the tendency of such feeds to elevate coke production and yield undesirable products have also led to new methods of contacting the feeds with catalyst. The methods of contacting FCC catalyst for very short contact periods have been of particular interest. Thus, short contact times of less than 3 seconds in the riser, and ultra short contact times of 1 second or less have shown improvements in selectivity to gasoline while decreasing coke and dry gas production.

To compensate for the continuing decline in catalyst to oil contact time in FCC processing, the "equilibrium" catalysts in use have tended to become more active. Thus, increases in the total surface area of the catalyst need to be achieved and as well, the level of rare earth oxide promoters added to the catalysts are increasing. Moreover, cracking temperatures are rising to compensate for the reduction in conversion. Unfortunately, it has been found

that the API gravity of the bottoms formed during short contact time (SCT) often increases after a unit revamp, leading some to suggest that the heaviest portion of the hydrocarbon feed takes longer to crack. Further, while a high total surface area of the catalyst is valued, the FCC process still values attrition resistance. Accordingly, while not obvious to those participating in the art, it has become increasingly likely that an optimization of FCC catalysts for the new short contact time and ultra short contact time processing which is presently being used is needed.

It is now theorized, that under the short contact time processing of hydrocarbons, that further improvements can be gained by eliminating diffusion limitations that may still exist in current catalysts. This is being concluded even as these materials excel at the application. It is theorized that improvements in these catalysts may be produced by optimization of catalyst porosity and the elimination of active site occlusion and diffusional restrictions of the binder phases present in catalysts prepared by the so-called incorporation method.

While the present assignee has produced zeolite microspheres with increased zeolite content and increased activity by increasing the macroporosity of the spray dried microsphere-zeolite precursors, the porosity of the formed zeolite microsphere catalysts has not before been considered a problem since there has been found no diffusion limitation under the previous FCC processing techniques. For example, commonly assigned, U.S. Patent No. 4,965,233, to Speronello discloses increasing the zeolite content of an in-situ catalyst by forming highly porous precursor microspheres, which allow increased amounts of zeolite to grow within the

porous matrix. The highly porous precursor microspheres are formed by spray drying a slurry of hydrous kaolin clay, which is characterized by the presence of a major amount of large (greater than 2 microns) kaolin stacks along with spinel calcined clay. When spray dried, the coarse hydrous kaolin results in microspheres having a desired high content of macropores in which the zeolite Y can grow. Likewise, commonly assigned, U.S. Patent No. 5,023,220, to Dight, et. al. also increases the macroporosity of the precursor microspheres by spray drying a mixture of hydrous clay, metakaolin and spinel. These catalyst microspheres have a substantial level of zeolite and are very active and selective. Further, the high alumina, silica-alumina matrix portion of the catalysts is often totally surrounded by the zeolite formed in-situ such that the matrix is only now understood to provide a reduced level of bottoms cracking under the short contact time FCC conditions.

Therefore, it is an object of the invention to provide a catalyst and a method for reproducibly preparing the same, wherein the catalyst is an attrition resistant, highly porous catalyst with a zeolite-coated matrix morphology.

It is another object of the invention to provide a catalyst and a method of making same, wherein the catalyst is provided with improved sodium removal characteristics, such that low sodium values are readily and consistently achieved.

It is another object of the invention to provide a catalyst optimized for short contact time FCC, particularly one that maximizes bottoms cracking and minimizes slurry gravity to levels at least as low as before an SCT revamp, without a dry gas penalty.

It is another object of the invention to provide a catalyst optimized for short contact time FCC, particularly one that allows the user to realize the full coke selectivity reduction benefits of SCT hardware.

5 It is another object of the invention to provide a catalyst optimized for short contact time FCC, particularly one that maximizes gasoline yields.

SUMMARY OF THE INVENTION

10 In accordance with this invention, novel zeolite microspheres are formed which are macroporous, have sufficient levels of zeolite to be very active and are of a unique morphology to achieve effective conversion of hydrocarbons to cracked gasoline products with improved
15 bottoms cracking under SCT FCC processing. The novel zeolite microspheres of the invention are produced by novel processing, which is a modification of technology described in U.S. Patent No. 4,493,902. It has been found that if the non-zeolite, alumina-rich matrix of the catalyst is derived
20 from an ultrafine hydrous kaolin source having a particulate size such that 90 wt. % of the hydrous kaolin particles are less than 2 microns, and which is pulverized and calcined through the exotherm, a macroporous zeolite microsphere can be produced. More generally, the FCC catalyst matrix useful
25 in this invention to achieve FCC catalyst macroporosity is derived from alumina sources, such as kaolin calcined through the exotherm, that have a specified water pore volume, which distinguishes over prior art calcined kaolin used to form the catalyst matrix. The water pore volume is
30 derived from an Incipient Slurry Point (ISP) test, which is described below.

The morphology of the microsphere catalysts which are formed is unique relative to the in-situ microsphere catalysts formed previously. Use of a pulverized, ultrafine hydrous kaolin calcined through the exotherm yields in-situ zeolite microspheres having a macroporous structure in which the macropores of the structure are essentially coated or lined with zeolite subsequent to crystallization. Macroporosity as defined herein means the catalyst has a macropore volume in the pore range of 600 - 20,000 Å of at least 0.07 cc/gm mercury intrusion. The catalysts of this invention should also have a BET surface area less than 500 m²/g. The novel catalyst of this invention is optimal for FCC processing, including the short contact time processing in which the hydrocarbon feed is contacted with a catalyst for times of about 3 seconds or less.

In the broadest sense, the invention is not restricted to macroporous catalysts having a non-zeolite matrix derived solely from kaolin. Thus, any alumina source which has the proper combinations of porosity and reactivity during zeolite synthesis and can generate the desired catalyst macroporosity and morphology can be used. The desired morphology comprises a matrix which is well dispersed throughout the catalyst, and the macropore walls of matrix are lined with zeolite and are substantially free of binder coatings. Accordingly, not only is the large pore surface area of the catalyst vastly improved over previous catalysts, and the active matrix dispersed throughout the microsphere, the zeolite crystals are readily accessible to the hydrocarbon feed. While not wishing to be bound by any theory of operation, it appears that previous catalysts in which the zeolite is incorporated into a matrix by physical mixing and glued with binder have sufficient macroporosity,

however the binder coats the active zeolite catalyst thereby blocking accessibility thereto. The present microsphere catalysts have a morphology which allows fast diffusion into the catalyst due to the macroporosity and enhanced
5 dispersion of the matrix, and further provides the highest accessibility to the zeolite inasmuch as the zeolite is freely coated onto the walls of the pores. The term "freely" means that the zeolite phase is present on the surface of the matrix and is unobstructed by any binder
10 phases. Merely having macroporosity does not provide the results we have obtained, since conventional incorporated catalysts have similar macroporosity. It is therefore the combination of porosity and zeolite-coated macropore walls that give the surprising selectivity results.

15 One would not have anticipated that contacting a heavy hydrocarbon feed, whose molecules are frequently if not generally too large to enter zeolite pores, with zeolite prior to feed contact with the matrix would be optimal, as has been found. Indeed, the prevailing "staged cracking"
20 theory suggests the opposite, that the larger hydrocarbon molecules are first cracked on the active matrix and the formed smaller molecules subsequently cracked within the zeolite. Much research and promotional activity has been done in pursuit or support of this perceived ideal.

25

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is an SEM photograph of the zeolitic microsphere of this invention as prepared in Example 6.

Figure 2 is a graph showing the nitrogen hysteresis
30 loops of the inventive catalyst and comparative catalyst.

Figure 3 is a graph of yield deltas found with an inventive catalyst relative to a conventional catalyst.

Figure 4 illustrates the gasoline yields from the tests shown in Figure 3.

DETAILED DESCRIPTION OF THE INVENTION

5 The catalyst microspheres of this invention are produced by the general process as disclosed in commonly assigned U.S. Patent No. 4,493,902. Importantly, the non-zeolitic, alumina-rich matrix of the catalysts of the present invention is preferably derived from a hydrous
10 kaolin source that is in the form of an ultrafine powder in which at least 90 wt. % of the particles are less than 2.0 microns, preferably at least 90 wt. % less than 1 micron. The ultrafine hydrous kaolin is pulverized and calcined through the exotherm. Typical zeolite microspheres have
15 been formed with an alumina-rich matrix derived from kaolin having a larger size than used in this invention and which is calcined at least substantially through its characteristic exotherm. Satintone® No. 1, (a commercially available kaolin that has been calcined through its
20 characteristic exotherm without any substantial formation of mullite) is a material used initially on a commercial basis to form the alumina-rich matrix. Satintone® No. 1 is derived from a hydrous kaolin in which 70% of the particles are less than 2 microns. Other sources used to form the
25 alumina-rich matrix include finely divided hydrous kaolin (e.g., ASP® 600, a commercially available hydrous kaolin described in Engelhard Technical Bulletin No. TI-1004, entitled "Aluminum Silicate Pigments" (EC-1167)) calcined at least substantially through its characteristic exotherm.
30 Booklet clay has found the most widespread commercial use and has met tremendous success worldwide. Before the

present invention, these larger clay particles represented the state of the art in forming the alumina-rich matrix of the catalyst microsphere and had no perceived deficits.

While the procedure for forming an in-situ zeolite
5 microspheroïdal catalyst as described in U.S. Patent No. 4,493,902, is essentially followed, the alumina-rich matrix, however, is derived from an ultrafine hydrous kaolin. What is meant by "ultrafine" powder is that at least 90 wt. % of the hydrous kaolin particles must be less than 2 microns in
10 diameter, preferably less than 1 micron determined by Sedigraph™ (or sedimentation). It has been found that, in particular, use of hydrous kaolin pigments with this particle size distribution upon pulverization and calcination through the characteristic exotherm results in a
15 greater quantity of macroporosity even in the catalyst microsphere subsequent to zeolite crystallization. The loose packing of the calcined ultrafine kaolin, which has been found, can be likened to a "house of cards" in which the individual particulates are aligned randomly with
20 respect to adjacent particles in a non-parallel manner. Moreover, the calcined ultrafine kaolin exists as porous aggregates of the "house of cards" morphology, providing not only a porous aggregate but additional porous areas between aggregates. Pulverization of the ultrafine hydrous kaolin
25 is required to provide the random stacking of the individual kaolin platelets.

Kaolin clays or pigments are naturally-occurring hydrated aluminum silicates of the approximate formula $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot \text{XH}_2\text{O}$, wherein X is usually 2. Kaolinite,
30 nacrite, dickite and halloysite are species of minerals in the kaolin group. It is well-known that when kaolin is

heated in air, that a first transition occurs at about 550° C. associated with an endothermic dehydroxylation reaction.

The resulting material is generally referred to as metakaolin. Metakaolin persists until the material is
5 heated to about 975° C. and begins to undergo an exothermic reaction. This material is frequently described as kaolin, which has undergone the characteristic exothermic reaction. Some authorities refer to this material as a defect aluminum-silicon spinel or as a gamma alumina phase. See
10 Donald W. Breck, Zeolite Molecular Sieves, published by John Wiley and Sons, 1974, pp. 314-315. On further heating to about 1,050° C., high temperature phases including mullite begin to form. The extent of conversion to mullite is dependent on a time-temperature relationship and the
15 presence of mineralizers, as is well-known in the art.

In the preferred embodiments of this invention, the pulverized ultrafine hydrous kaolin used to derive the alumina-rich matrix is calcined through its characteristic exotherm with or without the formation of mullite. An
20 especially preferred matrix source which is used in this invention to form the macroporous zeolite microspheres is Ansilex® 93. Ansilex® 93 is made from the fine size fraction of a hard kaolin crude, by spray drying, pulverizing and calcining to prepare low abrasion pigments
25 as described in U.S. Patent No. 3,586,523, to Fanselow, et. al., the entire contents of which are herein incorporated by reference. The ultrafine hydrous matrix source is spray dried, pulverized and then calcined through the exotherm, optionally to mullite. The aforementioned U.S. Patent No.
30 4,493,902 discloses calcining the kaolin clay to mullite until the X-ray diffraction intensities are comparable to a fully crystalline reference standard. While it is within

the scope of the present invention to calcine the kaolin beyond the exotherm such that the X-ray diffraction intensities are comparable to a fully crystalline referenced standard as disclosed in the '902 patent, it is preferred to calcine the kaolin beyond the characteristic exotherm so as to convert the kaolin to small crystallite size mullite. The small crystallite size mullite has the appropriate diffractional lines and leached chemical composition of a fully crystalline mullite standard, but the diffractional lines are weaker inasmuch as the crystallites are smaller. The relationship between diffraction intensity/line width and crystallite size is well-known. It is preferred to calcine the kaolin beyond the exotherm to a small crystallite mullite matrix inasmuch as fully calcining the kaolin to mullite takes excessive time and temperature in practice. Furthermore, calcining kaolin beyond the exotherm to fully crystalline mullite can result in the macroporosity being lost due to sintering. Moreover, the ISP and bulk density after calcining kaolin to fully crystalline mullite can be substantially increased. Thus, it is preferred that the ultrafine kaolin calcined through the exotherm has 20-80% of the integrated X-ray diffraction peak areas of a kaolin reference sample containing well crystallized mullite. More preferably, the ultrafine kaolin is calcined through the exotherm such that it has 50-70% of the integrated X-ray diffraction peak areas of fully crystallized mullite.

What is unusual about the use of the Ansilex® material is that it is derived from hard kaolin clay. Hard kaolin clays typically have a gray tinge or coloration and are, thus, also referred to as "gray clays". These hard kaolins are further characterized by breaking into irregularly

shaped fragments having rough surfaces. Hard kaolin clays also contain a significant iron content, typically about 0.6 to 1 wt. % of Fe_2O_3 . Hard kaolin clays are described in Grim's "Applied Clay Mineralogy", 1962, McGraw Hill Book Company, pp. 394-398 thereof, the disclosure of which is incorporated by reference herein. The use of these materials to form the alumina-rich matrix for in situ FCC microsphere catalysts has not been known previous to this invention, although their use in the incorporated routes is well established. Hard kaolin clays have also occasionally been used as sources of metakaolin for in situ microspheres, but not with advantage. Without wishing to be bound by any theory, it would appear that previous use of the calcined gray clays in the in situ matrix art would be precluded by (a) the high iron content thereof and the possibility that this could lead to coke and gas production, and (b) the dilatant nature of slurries formed therefrom, leading to apparently senseless waste of process time and increased cost in making down high viscosity slurries which spray dry at low solids. We now believe these dilatancy problems and porosity benefits are intrinsically and fundamentally linked. As for the former point, reduced coke and gas was an especially sought-after object for in situ catalysts, since the original formulations of Haden made coke and gas commensurate with their extraordinarily high level of amorphous matrix activity. This led to lower and lower levels of iron and spinel in subsequent inventions. We have made the surprising finding that there appears to be no relationship between the iron and coke and gas selectivities after all.

The alumina-rich matrix can be derived from alumina-containing materials more generally characterized by the

porosity thereof provided during the packing of the calcined material. A test has been developed to determine the pore volume of the calcined alumina-containing material which ultimately forms the matrix of the inventive catalyst. The test characterizes the water pore volume of the calcined alumina-containing material by determining the minimum amount of water needed to make a slurry from a sample of the solids. In the test, a powder sample is mixed with water containing a dispersant such as, for example, Colloid 211, Viking Industries, Atlanta, GA, in a cup using a stirring rod or spatula. Just enough water is added to the dry sample to convert the dry powder to a single mass of dilatant mud which only just begins to flow under its own weight. The incipient slurry point (ISP) is calculated from the weights of the sample and water used. The incipient slurry point can be calculated as follows:
$$\text{ISP} = \left[\frac{\text{grams of dry sample}}{\text{grams of dry sample plus grams of water added}} \right] \times 100.$$
 The units are dimensionless and are reported as percent solids.

This amount of water is larger than the (internal) water pore volume of the sample, but is clearly related to the water pore volume. Lower incipient slurry point percent solids values indicate higher water absorption capacities or higher pore volume in the sample. The calcined alumina-containing materials from which the high-alumina matrix is derived in accordance with this invention will have incipient slurry points less than 57% solids, preferably 48 to 52% solids. This compares with Satintone® No. 1 which yields over 58% solids in the incipient slurry point test.

Accordingly, not only is the ultrafine hydrous kaolin useful as an alumina-containing material from which to derive the matrix of the catalyst microspheres, but the

matrix may also be derived from delaminated kaolin, platelet alumina and precipitated alumina. Means for delaminating booklets or stacks of kaolin are well-known in the art. Preferred are those methods, which use a particulate
5 grinding medium such as sand, or glass microballoons as is well-known. Subsequent to delamination, the platelets are pulverized to derive the random packing or "house of cards" morphology.

The pulverize-calcine-pulverize processing of hydrous
10 kaolin is preferred to make the matrix precursor of the invention because it appears that, when the foregoing is used with hydrous kaolin as the metakaolin source to form the reactive precursor microspheres, superior attrition resistance results at high pore volume. While less
15 preferred, matrix precursors may also be wet milled to further de-agglomerate the precursor. The milling appears to reduce microsphere pore volume, all other things held constant. A method to reduce microsphere pore volume is useful when pre-calcined metakaolin powder is used to form
20 the reactive precursor microspheres. Dight has disclosed that employing metakaolin powder increases precursor microsphere pore volume, but excessive levels of zeolite and surface area can be required to make these microspheres acceptably attrition resistant. While helping to moderate
25 the required zeolite content and also perhaps improving the dispersion of said milled matrix in the microsphere, the de-agglomeration appears to have the effect of breaking strong bonds which could have otherwise strengthened the final catalyst, and so is not preferred.

30 It is also within the scope of this invention to derive the matrix from chemically synthesized spinel and/or mullite. Thus, Okata, et al., "Characterization of spinel

phase from $\text{SiO}_2\text{-Al}_2\text{O}_3$ xerogels and the formation process of mullite", Journal of the American Ceramic Society, 69 [9] 652-656 (1986), the entire contents of which are incorporated herein by reference disclose that two kinds of xerogels can be prepared by slow and rapid hydrolysis of tetraethoxy silane and aluminum nitrate nonahydrate dissolved in ethanol. The slow hydrolysis method involves gelling the above mixture in an oven at 60° C. for one to two weeks whereas the rapid hydrolysis method involves adding ammonium hydroxide solution to the mixture and drying in air. Xerogels prepared by the slow hydrolysis method crystallized mullite directly from the amorphous state on firing whereas the xerogels formed by rapid hydrolysis crystallized a spinel phase before mullite formation. As long as such calcined synthetic materials have a water pore volume within the scope of this invention, such materials can be used to derive the high-alumina matrix of the catalyst of this invention.

Preferably, the pore volume of the crystallized zeolite microsphere of this invention, which is formed using the high water pore volume alumina-containing materials as determined by the ISP test to form the catalyst matrix, is greater than 0.27 cc/gm, preferably greater than 0.30 cc/gm of Hg in the range of 40-20,000Å diameter. More particularly, the catalyst of this invention has a macropore volume within pores having a size range of 600 to 20,000Å of at least 0.07 cc/gm of Hg, and preferably at least 0.10 cc/gm of Hg. While conventional zeolite-incorporated catalysts have macroporosities comparable to the catalysts of this invention, the incorporated catalysts do not have the novel zeolite-on-matrix morphology nor performance of the catalysts of this invention. The catalysts of this